

HYDRODESULFURIZATION IN THE SOLVENT REFINED COAL PROCESS

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The Solvent Refined Coal (SRC) process is currently recognized as one of the more promising processes for producing an environmentally acceptable boiler fuel from coal. In the SRC process, coal is liquefied to allow removal of entrained mineral matter by physical separation methods and reacted with hydrogen to remove chemically part of its organic sulfur. Liquefaction of coal has been shown to occur almost instantaneously upon reaching reaction temperatures while in the presence of a hydrogen-donor solvent, the overall rate limiting step in liquefaction being rehydrogenation of process solvent - which may be performed separately in the recycle stream - to replenish hydrogen-donor species (1,2). Based on data collected in this laboratory hydrodesulfurization (HDS) of coal, on the other hand, appears to be a much slower reaction. As a result, the kinetics of HDS will be a primary, if not the controlling factor in the design and operation of the dissolver/reactor in the SRC process.

In the present work, an experimental evaluation is made of the feasibility for accelerating HDS of coal by simply varying reaction conditions and utilizing coal mineral matter and/or other cheap regenerable catalysts. The rate data reported were all obtained in a batch system; and, except for one series of experiments, only one coal type, a bituminous Kentucky No. 9/14, was used. Experimental methods and materials are given in (2), except as noted herein. A reaction model was developed that gives an excellent fit to the experimental data. The model, as well as other results of the comparative studies performed, is intended to assist in predicting and interpreting results from pilot studies of the SRC process, such as those at Wilsonville, Alabama, and Tacoma, Washington. The model provides also a useful design tool; but, for a reaction system as complex as the one dealt with here, it would be presumptuous to suggest that it represents the true mechanism.

In a previously reported catalyst screening study (5), several minerals indigenous to coal were shown to have a catalytic effect on the HDS of creosote oil. Of particular interest was the observation that in the presence of reduced metallic iron the HDS rate of the oil was significantly higher than that resulting when no mineral was present; whereas, in the presence of pyrite the HDS rate was about the same as it was when no mineral was present. These observations were surprising in that both reduced iron and pyrite are converted into the sulfide form (pyrrhotite) within the first fifteen to twenty minutes of reaction. Based on these observations, to further examine the practicality of coal mineral catalysis, a series of experiments was performed to ascertain whether the acceleration of the HDS rate in the presence of iron was predominantly thermodynamic or catalytic in nature. It is possible that iron, by removing H_2S , promotes HDS by Le Chatelier's principle, or simply prevents the H_2S from reducing the activity of catalytic sulfides by preferential adsorption.

Basic Nature of Reactions

The influent coal/oil slurry to the reactor/dissolver in the SRC process includes a wide variety of sulfur-containing compounds; thiols, disulfides, sulfides, thioethers, γ -thiopyrone, thiophenes, dibenzothiophenes, and other heterocyclic sulfur compounds. In general, thiols, disulfides, sulfides, thioethers, and γ -thiopyrone are very reactive - undergoing hydrogenolysis at an appreciable rate, forming H_2S and hydrogenated compounds, without the aid of a catalyst; whereas, heterocyclic sulfur compounds are much less reactive - requiring a catalyst to achieve an acceptable HDS rate. As a result of the large difference in reactivity of these two groups of sulfur-containing

compounds and to simplify analysis, the HDS reactions involving individual compounds in each of these two groups sometimes are lumped together; and HDS of a coal/oil slurry is often treated as if there were only two reactive compounds (3,4).

In addition to HDS reactions, under reaction conditions used in the SRC process, hydrocracking (i.e., breaking of C-C bonds) and hydrogenation reactions also occur. It is by means of these reactions - particularly cracking reactions - that coal solids are converted into lower molecular weight components that are soluble in SRC process solvent, allowing removal of entrained mineral matter by subsequent physical separation methods. These reactions take on importance, other than liquefaction of coal solids, by consuming hydrogen in the process without removing sulfur. Only that amount of hydrogenation, or cracking, required to liquefy coal solids and allow mineral matter removal is desired. Any excess hydrogenation beyond this amount, such as in the formation of C_1 - C_4 gases, etc., results in inefficient use of hydrogen, thus higher operating costs. This should be avoided as much as possible. Actually SRC product contains a slightly lower hydrogen/carbon ratio ($H/C = 0.75$) than the feed coal itself ($H/C = 0.8$). Furthermore, the stoichiometric amount of hydrogen required solely for removal of an acceptable amount of sulfur as H_2S in the SRC process is an order-of-magnitude less than the total amount of hydrogen currently consumed (two weight per cent of MAF coal feed) at the Wilsonville, Alabama, and the Tacoma, Washington, SRC pilot plants. Excess hydrogenation therefore accounts for most of the hydrogen consumed in producing solvent refined coal.

The rate of noncatalytic (except for mineral matter) HDS, unlike that of hydrogenation, appears to be relatively insensitive to hydrogen concentration, in the form of either dissolved molecular hydrogen or readily transferable hydrogen such as that attached to donor species (e.g., tetralin) contained in the process solvent. Variation, for example, in initial hydrogen partial pressure from 1000 to 2600 psig at reaction temperature had no significant effect on the final organic sulfur content of a coal/creosote-oil reaction mixture, even after two hours of reaction (Table 1). Also, as shown in Table 2, the reduction in total sulfur content of the coal was essentially the same after fifteen minutes of reaction when slurried with creosote oil - which contained only trace amounts of tetralin and other known hydrogen-donor species - as when slurried with pre-hydrogenated creosote oil - which, like the SRC recycle oil used, contained significant amounts of tetralin and 9,10 dihydrophenanthrene. The rate of liquefaction, on the other hand, was significantly higher when the coal was extracted in prehydrogenated creosote oil. When reacted in an inert nitrogen atmosphere, the cresol-soluble yield was almost twice that obtained when the coal was extracted with untreated oil. The high sensitivity of the rate of liquefaction, as opposed to the relative insensitivity of HDS to hydrogen concentration is further evidenced in that the cresol-soluble yield was significantly higher when the coal was reacted in an initial 2000 psi hydrogen atmosphere, both when slurried with creosote oil and also when slurried with pre-hydrogenated creosote oil. Also, solvent-to-coal ratio had no significant effect on HDS rate relative to that of liquefaction (Table 3).

The rate limiting step in liquefaction has been shown to be the reaction of dissolved molecular hydrogen with the donor solvent, with the transfer of hydrogen from the donor solvent to coal solids occurring rapidly (1,2). In fact, when extracted in a highly active hydrogen donor solvent such as hydrogenated creosote oil, coal solids have been observed to liquefy almost instantaneously upon reaching reaction temperature (1). Thus the observed sensitivity of the rate of liquefaction to hydrogen concentration should be expected. Furthermore, as long as solvent quality (i.e., a sufficiently high hydrogen-donor concentration) is maintained - which can be done independently by hydrogenating the recycled process

solvent as is done in the Exxon process - with liquefaction occurring almost instantly. HDS should be the controlling factor in the design and operation of the dissolver/reactor. HDS kinetics thus take on a special importance for the commercialization and development of the SRC process.

Coal Mineral Catalysis

A limited experimental evaluation of process advantages and disadvantages of coal mineral catalysis was presented in an earlier work (5). As part of this evaluation, twelve different coal minerals and, also, actual SRC mineral residue as well as coal ash were individually screened to rate their catalytic activity on the HDS rate and hydrogenation of creosote oil relative to that of a commercial Co-Mo-Al catalyst. Some results of this earlier work are given in Table 4 and in Figures 1 and 2. Reduced iron, reduced pyrite (presumably pyrrhotite), and pyrite had decreasing effects on sulfur removal during hydrogenation/hydrodesulfurization of creosote oil at 425°C, with reduced iron being second only to Co-Mo-Al in catalytic activity for HDS and with pyrite, despite its pronounced effect on hydrogenation, having essentially no apparent catalytic activity for HDS. The relatively insignificant effect of pyrite on HDS rate was further evidenced in that the rate of organic sulfur removal from coal slurried in creosote oil remained essentially the same even after about seventy-five per cent of its pyritic content had been removed physically by magnetic separation prior to reaction (Figure 3). Reduced iron, on the other hand, was found to have a significant effect on HDS reactions when present in only trace amounts (Table 5).

The stable form of iron in the presence of hydrogen and hydrogen sulfide in the temperature range of 400 to 500°C is pyrrhotite (6,7). As shown in Figure 4, pyrite is reduced to the sulfide (presumably pyrrhotite) within about fifteen minutes of reaction at 425°C. Rapid reduction of pyrite coal minerals has also been observed to occur in the dissolver/reactor at the Wilsonville SRC pilot plant (8). H₂S product from the reduction of pyrite is thus generated in the early stages of HDS. H₂S is known to inhibit catalytic HDS of petroleum feedstocks; thus, since some of the same sulfur-containing components in petroleum feedstocks exist also in coal/oil slurries, H₂S may inhibit HDS of coal/oil slurries, or possibly react with previously desulfurized components. Therefore, since reduced iron acts as an H₂S scavenger, instead of an H₂S producer as does pyrite, one possible reason for the differences in catalytic activities of reduced iron, reduced pyrite, and pyrite could be the different amounts of H₂S present during HDS as is shown in Table 4. In fact, the H₂S partial pressure was increased by a magnitude of two to three by the reduction of pyrite; whereas no traceable amount of H₂S product was present during the reduced iron run. Also, when different weight percentages of iron were charged with creosote oil (Table 5), no H₂S product was detected until less than one per cent by weight of iron was present. Interestingly enough, when iron was present in higher weight percentages (2.4 to 20%), the amount of sulfur removed during reaction was only slightly different, and when present in lower percentages (1.0 to 0.5%), it decreased in proportion to the amount of iron present, with trace amounts of iron being as effective as 0.5 weight percent. The retarding effect of H₂S on HDS is further evidenced in that when H₂S was added prior to reaction the amount of sulfur removed was less during hydrogenation/HDS of both a bituminous Kentucky No. 9/14 mixture coal and a sub-bituminous (Wyodak) coal (Table 10).

When iron gauze was used to scrub out any H₂S product formed during hydrodesulfurization of creosote oil, while being mounted in the top of the reactor above the oil, the amount of sulfur removal was about 20% higher than that obtained without any scavenger agents present; that is, the final sulfur content of the oil was 0.39% as opposed to 0.50%, a decrease equivalent to that obtained when one

weight percent of iron was present. Apparently then, H_2S does have a retarding effect on HDS as might be expected from thermodynamics.

When five weight percent iron and a sufficient amount of H_2S (to prevent its complete removal by reaction) were present during HDS of creosote oil, the amount of sulfur removal was only the same as that when either a trace amount or a half weight percent of iron was present (Table 5). Apparently H_2S retards the effectiveness of iron sulfide as a catalyst, with trace amounts of iron sulfide having about the same catalytic effect on HDS rates as larger amounts when an appreciable H_2S atmosphere exists. Since H_2S does have a thermodynamic effect on the HDS reactions; however, the severity of its catalytic inhibition effect is not completely defined.

In summary then, reduced iron appears to favor HDS by scavenging H_2S product, preventing any reverse reactions and by catalyzing HDS reactions. Unfortunately, as shown in Table 6, reduced iron, like most HDS catalysts, also accelerates hydrogenation; as a result its use as a catalytic agent in the SRC process could contribute to excess hydrogenation. Because of its potential as an inexpensive HDS catalyst, however, further experiments are now in progress to better evaluate its role in accelerating HDS reactions and its selectivity for HDS versus hydrogenation.

Hydrodesulfurization Kinetics in the SRC Process

As shown in Figure 5, the variation of organic sulfur content of a coal/creosote-oil reaction mixture with time follows a path close to that expected for an overdamped second order dependence of rate on organic sulfur content. This kinetic behavior is consistent with the basic nature of HDS reactions as described in the foregoing discussion, in that it can be modelled by considering the reaction mixture to contain only two hypothetical sulfur-containing compounds with significantly different rate constants. The desulfurization reaction of each of the two hypothetical components is assumed to follow first-order kinetics. A test as to whether this assumed kinetic model is representative is the difference in magnitude of the experimental rate constants, for the actual two groups of lumped sulfur components are known to react at two widely differing rates. The large difference in slope of the two lines in Figure 6 indicates that the experimental rate constants are indeed significantly different, attesting that the model is representative.

The high sensitivity of HDS rate to reaction temperature and its low sensitivity to hydrogen concentration suggested that the HDS reactions were chemically controlled and pseudo-homogeneous kinetics were thus used in modeling. Furthermore, since the retarding effect of H_2S and the catalytic effect of pyrite coal minerals apparently either offset each other or exist to such an extent that the effect on HDS rate is insignificant - as a first-hand approximation-no kinetic terms were used to represent the reverse reaction by H_2S product. The rate equation was thus written as:

$$r_{HDS} = -K_1 S_1 - K_2 S_2 \quad (1)$$

where: S_1 , and S_2 are the organic sulfur concentration (g/cc) present in the form of the two hypothetical sulfur-containing components, respectively. For a batch reactor,

$$S = S_{10} e^{-K_1 t} + S_{20} e^{-K_2 t} \quad (2)$$

The adjustable parameters S_{10} , S_{20} , K_1 and K_2 were determined empirically, using a nonlinear minimum sum-of-the-squares numerical search routine. The Arrhenius relationship was assumed, and rate data for three different reaction temperatures were used in determining empirical values for the four adjustable parameters. A list of these values is given in Table 7; and a comparison between predicted HDS paths and rate data is made in Figure 5, showing good agreement. Also, the Arrhenius plots of the empirical rate coefficients are given in Figure 6. The rate coefficients for the two hypothetical components differ by two orders of magnitude (Table 8), in consistency with the large difference in slopes of the two straight lines in Figure 6. In addition, the high activation energy (Table 8) for the reactive sulfur-containing component provides further evidence that the desulfurization reactions are chemically, rather than mass transfer controlled. Note that there is no catalyst present, except for the indigenous coal mineral matter. Finally, as shown in Table 9, the energies and enthalpies of activation are indicative of chemical rate processes, rather than transport processes. The high activation energy and low entropy of activation for the fast reaction are indicative of a homogeneous reaction; the lower values for the slow reaction indicate a possible catalytic effect, perhaps due to coal mineral matter. Here again, however, since the exact reaction mechanism is unknown, one must exercise caution when attaching significance to these numerical values.

Conclusions

Hydrodesulfurization reactions occur, under reaction conditions used in the SRC process, at a rate that is practically independent of hydrogen concentration. Reduced iron has a catalytic effect on HDS reactions; in fact, it exhibits a significant memory effect. Because of additional H_2S product, pyrite has only a slight catalytic effect on HDS reactions. The retardation of HDS reactions by H_2S product is due to catalytic inhibition as well as thermodynamic effects. HDS reactions can be modeled as two first-order reactions occurring in parallel, with two widely different rate constants.

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Table 1

Reaction Temp., °C.	Reaction Time Min.	N ₂ TOTAL AND ORGANIC SULFUR IN REACTION MIXTURE				
		2600 PSI	2600 PSI	2600 PSI	1000 PSI	Average
		Total Organic	Total Organic	Total Organic	Total Organic	Total Organic
385	15	.85	.82	.94	.95	.82
410	15	.88	.75	.80	.81	.75
435	15	.81	.68	.82	.84	.69
385	30	.89	.76	.90	.89	.76
410	30	.81	.68	.83	.86	.75
435	30	.73	.63	.73	.80	.68
385	60	.81	.70	.87	.89	.76
410	60	.75	.65	.74	.86	.73
435	60	.73	.60	.74	.75	.60
385	120	.81	.68	.87	.89	.76
410	120	.75	.65	.74	.86	.73
435	120	.65	.53	.66	.69	.56

Table 2. Effect on Gaseous Hydrogen and Solvent Type on Liquefaction and Hydrodesulfurization of Coal

Solvent Type	Atmosphere (atm)	Conversion (Based on Cresol Solubles) %	Total Sulfur in Reaction Mixture	Total Sulfur in Solvent (±)	Total Sulfur in Total Solvent (±)
Cresote Oil	2000 psi H ₂	42.1	.90 ± .02	.5	2.0
Hydrogenated Cresote Oil	2000 psi H ₂	83.1	.49 ± .03	trace	2.0
Peacycle Oil (Sample No. 16171)	2000 psi H ₂	70.9	.73 ± .01	.25	2.1
Cresote Oil	2000 psi H ₂	61.0	.91 ± .05	.5	2.1
Hydrogenated Cresote Oil	2000 psi H ₂	90.7	.51 ± .03	trace	2.0
Peacycle Oil (Sample No. 16171)	2000 psi H ₂	85.8	.75 ± .02	.26	2.2

NOTE: Reaction Time = 15 min.
Solvent-to-Coal Ratio = 3/1
Reaction Temperature = 410°C

Table 3
Effect of Solvent/Coal Ratio on Hydrodesulfurization and Liquefaction

Solvent-to-Coal Ratio	Temperature (°C)	Conversion based on Cretol Solubles	Residual Organic Sulfur
1.5/1	410	84.5	1.45
2/1	410	85.3	1.39
3/1	410	90.7	1.55
3/1	385	80.4	1.66
4/1	385	83.6	1.81

Operating Conditions: 2,000 rpm
2,000 psig H₂

Reaction Time = 15 min.

Initial Organic Sulfur = 1.63

Table 4

CATALYST SCREENING RUNS:
LIQUID Σ SULFUR, TOTAL PRESSURE, AND FINAL GAS COMPOSITION

MINERAL	Σ S	TOTAL PRESSURE (10 ⁻³ PSI)	PARTIAL PRESSURES (PSI)				
			H ₂ (10 ⁻³)	H ₂ S	CO ₂	CH ₄	C ₂ -C ₅
NONE	0.52	2.40	2.13	10.	2.5	64.	18.
NONE	0.46	2.42	2.23	7.1	2.0	62.	24.
MUSCOVITE (-80)	0.39	2.18	1.94	8.5	1.0	51.	20.
PYRITE (-80, + 150)	0.41	1.99	1.54	230.	1.1	99.	36.
IRON (-325)	0.27	1.98	1.75	<1.	12.	16.	20.
REDUCED PYRITE	0.36	1.96	1.85	17.	0.4	61.	18.
COAL ASH	0.23	1.92	1.72	<1.	1.4	57.	15.3
SIDERITE	0.34	1.81	1.61	<1.	67.	93.	29.
SRC SOLIDS (-325)	0.32	1.73	1.48	13.	24.	85.	30.
PYRITE (-325)	0.55	1.63	1.22	196.	7.3	133.	71.
Co-Mo-AL (-80, + 150)	0.02	1.12	0.92	<1.	1.9	128.	74.
Co-Mo-AL (-325)	0.02	1.02	0.73	1.7	1.3	138.	79.

Table 5. Effect of Iron Concentration On
Hydrosulfurization of Creosote Oil

Iron Concentration (weight percent)	Final H ₂ S Partial Pressure (psi)	Residual Sulfur (percent)
20.	0.	.34
20.	0.	.34
13.	0.	.35
13.	0.	.36
13.	0.	.35
4.7	0.	.35
2.4	0.	.38
0.99	8.	.40
0.49	66.	.43
trace (memory effect)	63.	.42
trace (memory effect)	--	.45
0	36.	.50
0	67.	.50

Reaction Conditions:

Temperature = 425°C
H₂ Pressure = 3000 psig @ 425°C
Agitation Rate = 1000 rpm
Initial Sulfur Concentration = 0.64 percent
Reaction Time = 2 hours

Table 7
Hydrosulfurization Model Parameters

S ₁₀	1.53×10^{-3} g/cc
S ₂₀	6.51×10^{-3} g/cc
K ₁ (385°C)	1.69×10^{-2} min ⁻¹
K ₁ (410°C)	5.30×10^{-2} min ⁻¹
K ₁ (435°C)	15.32×10^{-2} min ⁻¹
K ₂ (385°C)	8.15×10^{-4} min ⁻¹
K ₂ (410°C)	13.89×10^{-4} min ⁻¹
K ₂ (435°C)	22.74×10^{-4} min ⁻¹

Table 8
Arrhenius Constants

ln K ₁₀	27.11	min ⁻¹
ln K ₂₀	7.417	min ⁻¹
ΔE ₁	40.78	kcal
ΔE ₂	18.99	kcal

Table 9
Comparison of Energies, Enthalpies, and Entropies
of Activation of Hydrosulfurization with Data
for Hydrosulfurization of Coal Tar over WS₂ Catalyst.*

Table 6: Comparison of Hydrogenation and Hydrosulfurization
of Creosote Oil in the Presence of Iron Catalyst

Wt. % Fe	(H/H ₀) _{AVG}	(S _F /S ₀) _{AVG}
0	0.80	0.78
0.5	0.71	0.63
1.0	0.74	0.62
2.4	0.74	0.58
4.7	----	0.55
13.0	0.69	0.56
20.0	0.64	0.52

	HDS Model		Coal Tar*
	Reaction 1	Reaction 2	
ΔE	40.7	38.9	11 kcal/mole
ΔH	39.2	15.8	9 kcal/mole
ΔS	-16.8	-58.2	-50 C.U.

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Table 10: Effect of H₂S on Rate of Hydrosulfurization
of Kentucky and Wyodak Coals

Atmosphere	Coal Type	Solvent Type	Solvent-to-Coal Ratio	Cresol Soluble Yield (%)	Total % Sulfur Before	Total % Sulfur After	% Sulfur Liquid Fraction	% Sulfur Solid Fraction
H ₂	Wyodak	Recycle	3:1	76.0	0.52	0.41	0.35	1.15
H ₂ + H ₂ S	Wyodak	Recycle	3:1	76.6	0.52	0.72	0.62	2.04
H ₂	Kentucky 9/14	Recycle	2:1	86.4	1.10	0.80	0.52	2.86
H ₂ + H ₂ S	Kentucky 9/14	Recycle	2:1	88.9	1.10	0.98	0.60	3.58

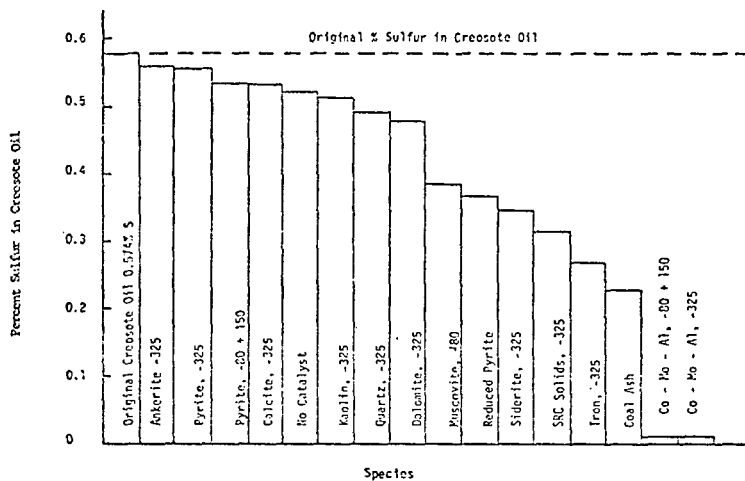


Figure 1. COMPARISON OF DESULFURIZATION ACTIVITY OF CATALYST

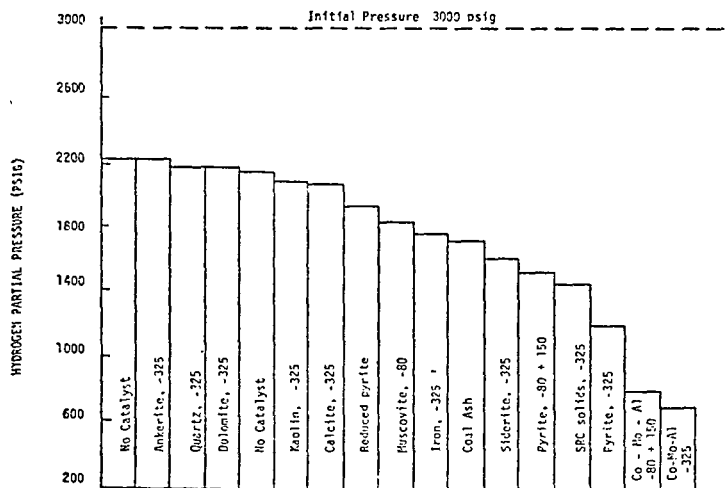
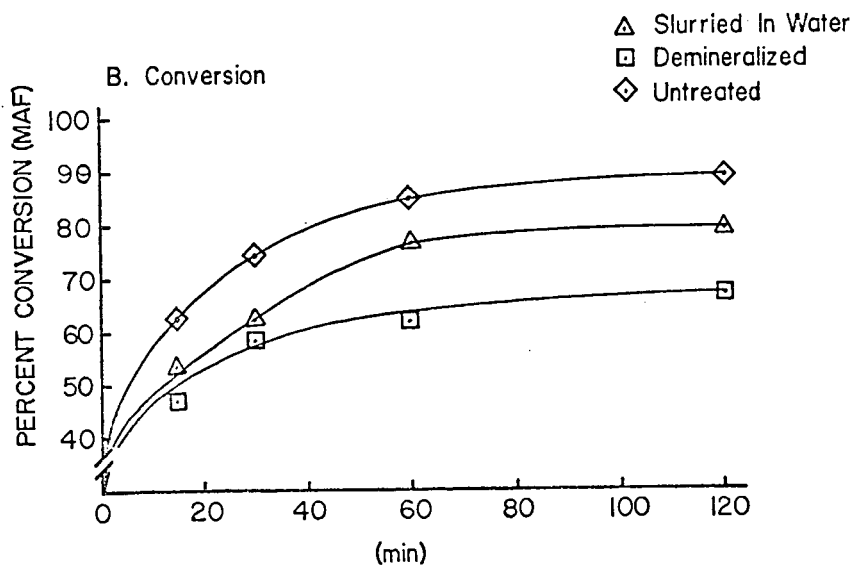
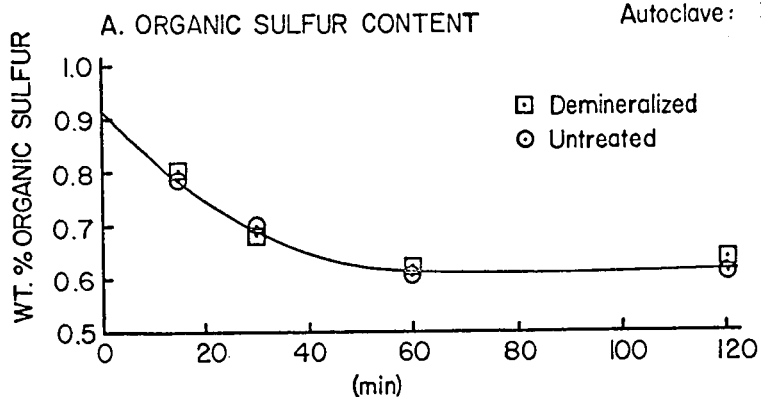


Figure 2. COMPARISON OF HYDROGENATION ACTIVITY OF CATALYST

Figure 3. Effect of Demineralizing Coal Feed and Slurrying Coal Feed with Water on Conversion

Temperature: 410° C
H₂ Pressure: 2000psig @ 410°C
Agitation Rate: 1000 rpm
Autoclave: 300 cc



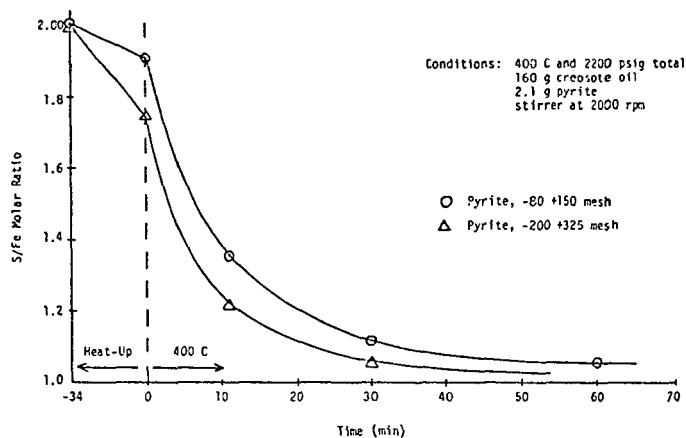


FIG. 4. PYRITE REDUCTION AS A FUNCTION OF TIME

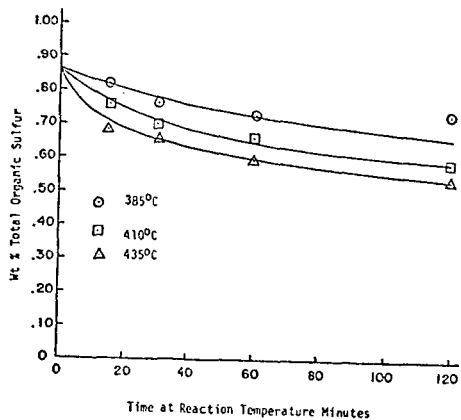


Figure 5. Effect of Reaction Temperature on Organic Sulfur Concentration

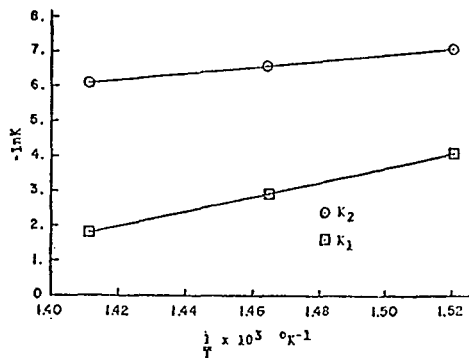


Figure 6. Arrhenius plot for hydrodesulfurization